

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 06-052871

(43)Date of publication of application : 25.02.1994

BEST AVAILABLE COPY

(51)Int.Cl.

H01M 8/02

H01M 4/86

H01M 8/10

(21)Application number : 05-131657

(71)Applicant : HITACHI LTD

(22)Date of filing : 02.06.1993

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(30)Priority

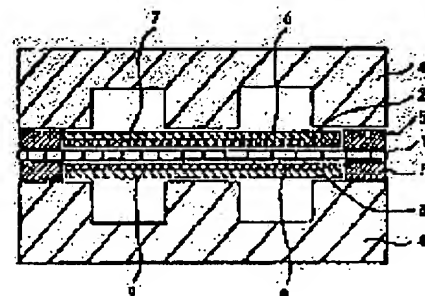
Priority number : 04165459 Priority date : 02.06.1992 Priority country : JP

(54) SOLID HIGHPOLYMER FUEL CELL

(57)Abstract:

PURPOSE: To greatly enhance the activity of an air electrode so as to significantly enhance the performance of a fuel cell having a hydrogen electrode and an air electrode provided on both sides of a film of solid highpolymer electrolyte by making the water repellency of the hydrogen electrode higher than that of the air electrode.

CONSTITUTION: A fuel cell comprises a hydrogen electrode 2 consisting of a catalyst layer 6 and a gas diffusion layer 7 with a film 1 of solid highpolymer electrolyte sandwiched therebetween, an oxygen electrode 3 consisting of a catalyst layer 8 and a gas diffusion layer 9, and a current collector 4 provided with several gas supply channels, and the end portion of each electrode 2, 3 is sealed by gas seals 5 to prevent gas leaks. Each of the catalyst layers is obtained by mixing and molding of an active component, a carbon carrier, a proton conductor and a water-repellent binding agent while the water repellency of the hydrogen electrode 2 is made higher than that of the oxygen electrode 3. Therefore, at the hydrogen electrode, electrode reactions in pores are accelerated, whereas at the oxygen electrode water is allowed to migrate easily and can readily be drained out of the system; so the gas diffusion properties of both of the electrodes are improved, resulting in enhancement of cell performance.



LEGAL STATUS

[Date of request for examination] 18.03.1996

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

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CLAIMS

[Claim(s)]

[Claim 1] The solid-state polyelectrolyte film, and the hydrogen pole and oxygen pole which is a gas diffusion electrode prepared so that the electrolyte membrane might be inserted, A means to supply hydrogen content gas and oxygen content gas to this hydrogen pole and this oxygen pole is provided. This gas diffusion electrode Carbon support, The polymer electrolyte fuel cell which consists of electronic conductors which served both as the catalyst bed and gaseous diffusion layer which consist of the active ingredient, the proton conductor, and the water-repellent binder which were supported by it, and is characterized by the water repellence of the catalyst bed by the side of this hydrogen pole being higher than the water repellence of the catalyst bed by the side of this oxygen pole.

[Claim 2] It is the polymer electrolyte fuel cell according to claim 1 characterized by the water repellence of the catalyst bed of a hydrogen pole and the catalyst bed of an oxygen pole being lower than each gaseous diffusion layer side a solid-state polyelectrolyte film side, and the water repellence by the side of the solid-state polyelectrolyte film of the catalyst bed of an oxygen pole being lower than the water repellence by the side of the solid-state polyelectrolyte film of the catalyst bed of a hydrogen pole.

[Claim 3] The amount of a water-repellent binder is the polymer electrolyte fuel cell according to claim 1 with which the amount of a hydrogen pole is characterized [in / about an oxygen pole, are 10 - 40 % of the weight, are 20 - 50 % of the weight about a hydrogen pole, and / the difference] by many [10% of the weight or more] things rather than the amount of an oxygen pole to the whole quantity of each catalyst bed of a hydrogen pole and an oxygen pole.

[Claim 4] The amount of a water-repellent binder is the polymer electrolyte fuel cell according to claim 1 with which the amount of a hydrogen pole is characterized [in / about an oxygen pole, are 10 - 30 % of the weight, are 20 - 40 % of the weight about a hydrogen pole, and / the difference] by many [10% of the weight or more] things rather than the amount of an oxygen pole to the whole quantity of each catalyst bed of a hydrogen pole and an oxygen pole.

[Claim 5] The amount of the water-repellent binder of the catalyst bed by the side of the solid-state polyelectrolyte film of a hydrogen pole is a polymer electrolyte fuel cell according to claim 2 characterized by many [10% of the weight or more] things in the difference rather than it by the side of the solid-state polyelectrolyte film of an oxygen pole.

[Claim 6] The polymer electrolyte fuel cell according to claim 1 characterized by the catalyst bed of a hydrogen pole having porosity smaller than the porosity of the catalyst bed of an oxygen pole.

[Claim 7] The polymer electrolyte fuel cell according to claim 3 which porosity is 35 - 60% about the catalyst bed of a hydrogen pole, and is characterized by being 40 - 65% about the catalyst bed of an oxygen pole.

[Claim 8] The catalyst bed of an oxygen pole and the catalyst bed of a hydrogen pole are a polymer electrolyte fuel cell according to claim 1 which is a multilayer more than two-layer, and is characterized by water repellence being higher a gaseous diffusion layer side in each catalyst bed, respectively.

[Claim 9] The polymer electrolyte fuel cell according to claim 1 characterized by the solid-state polyelectrolyte film consisting of perfluoro sulfonic acid type resin or perfluoro carboxylic acid type resin.

[Claim 10] An active ingredient is a polymer electrolyte fuel cell according to claim 1 characterized by consisting of a platinum metal.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to a polymer electrolyte fuel cell, especially relates to a solid-state polyelectrolyte mold hydrogen-oxygen fuel cell.

[0002]

[Description of the Prior Art] Generally a polymer electrolyte fuel cell possesses two charge collectors, solid-state polyelectrolyte film (only henceforth an "electrolyte membrane"), two electrodes that sandwich an electrolyte membrane, and a means to supply the hydrogen as a fuel, and the oxygen as an oxidizer. Two electrodes have the catalyst bed which consisted of a catalytic activity component, support which supports this catalytic activity component, an ion (proton) conductor of the same solid-state macromolecule as the above-mentioned electrolyte, and a binder which hardens these. two electrodes are with a hydrogen pole and an oxygen pole, and the electrochemical reaction which boils, respectively and can be set is as follows.

[0003] On a hydrogen pole, a hydrogen molecule is ionized, it becomes a proton and an electron is emitted.

[0004] A proton conducts the ion conductor in an electrode, reaches an electrolyte membrane, passes through the inside of an electrolyte membrane further, and moves to the oxygen pole of an opposite hand. On the other hand, the emitted electron moves to an oxygen pole through an external circuit. On the oxygen pole, a proton combines with the electron emitted from the hydrogen pole, and water is generated.

[0005] The reaction process of the above-mentioned fuel cell mainly consists of the following four phases.

[0006] (A) Conduction in the interior of the reaction on the front face of a catalyst in the diffusion to the catalyst front face of hydrogen and oxygen, (B) hydrogen pole, and an oxygen pole, the interior of two poles of the (C) proton, and an electrolyte, and bleedoff of (D) water.

[0007] Extent of diffusion of the fuel gas in each phase and extent of a reaction rate influence cell output characteristics greatly.

[0008] In the phase of the above (A), it is effective to perform efficiently supply on a catalyst front face and diffusion of a fuel, and using the carbon plate which has a rectangle slot which is indicated by a wave type charge collector as shown in drawing 1 of JP,60-35472,A, JP,3-102774,A, or JP,2-86071,A is proposed. If the side which has the slot of the carbon plate which has these wave type charge collectors and rectangle slots is contacted to an electrode, space will be generated in the contact surface and a fuel will be spread in an electrode surface through this space. In the polymer electrolyte fuel cell, the usually above structures are adopted and a certain amount of output is discovered.

[0009] A reaction with oxygen progresses by the interface of an electrolyte membrane and an oxygen pole, in an oxygen pole interface, water is generated, the water screen is especially formed with high current density, and the so-called flooding phenomenon produces the proton which has passed the electrolyte membrane. The contacting efficiency of the oxygen gas and the catalyst which have diffused the inside of an electrode for this water screen falls, reduction in output density becomes easy to take place, and the cell engine performance destabilizes. It is easy to produce especially this flooding phenomenon in the interface of an oxygen pole and an electrolyte. Then, it is necessary to remove this generation water out of a system.

[0010] Therefore, it has proposed controlling the water repellence of an electrode in U.S. Pat. No. 4,643,957, and canceling a flooding phenomenon.

[0011]

[Problem(s) to be Solved by the Invention] The object of this invention is offering the polymer electrolyte fuel cell which is made to promote migration of the proton generated from a hydrogen molecule on the hydrogen pole, and has the electrode structure of accelerating the oxidation reduction reaction produced in the interface of an electrode and an electrolyte membrane while preventing the flooding of water on the

oxygen pole and improving the contacting efficiency of an electrode catalyst bed and gas, in order to diffuse the gas of a hydrogen pole and an oxygen pole at high effectiveness.

[0012]

[Means for Solving the Problem] The hydrogen pole and oxygen pole which are a gas diffusion electrode prepared so that this invention might sandwich the solid-state polyelectrolyte film and its electrolyte, A means to supply hydrogen content gas and oxygen content gas to a hydrogen pole and an oxygen pole, respectively is provided. This gas diffusion electrode It consists of electronic conductors which served both as the catalyst bed and gaseous diffusion layer which consist of carbon support, an active ingredient supported by it, and a proton conductor and a water-repellent binder, and the water repellence of this catalyst bed is the polymer electrolyte fuel cell characterized by being higher than an oxygen pole side a hydrogen pole side.

[0013] According to this invention, the cell engine performance of a polymer electrolyte fuel cell can be raised by controlling the water repellence of the catalyst bed of each electrode under a certain specific condition.

[0014] According to an example of this invention, the electrolyte membrane of the water repellence of a hydrogen pole is lower than a gaseous diffusion layer, and similarly, the water repellence in the catalyst bed of an oxygen pole is also lower than a gaseous diffusion layer an electrolyte membrane side, and, moreover, lower [the water repellence by the side of the electrolyte membrane of the catalyst bed of an oxygen pole] than the water repellence by the side of the electrolyte membrane of the catalyst bed of a hydrogen pole. In addition, on both an oxygen pole and a hydrogen pole, although it is good as for one layer in a catalyst bed, the multilayer more than two-layer is sufficient.

[0015] According to this invention, the catalyst bed of the two poles of a hydrogen pole and an oxygen pole consists of carbon support, the active ingredient (catalyst) supported by it and a proton conductor, and a water-repellent binder. As for an active ingredient, it is desirable to be chosen out of platinum or a platinum metal, for example, a rhodium, a ruthenium, palladium, and iridium, and even if the construction material of a proton conductor is the same as a solid-state polyelectrolyte, it may differ again. Moreover, the graphites fluoride expressed with fluororesins, such as polytetrafluoroethylene (PTFE), or (CF) n and those mixture are suitable for a water-repellent binder.

[0016] Generally the electrolyte used by this invention is a membranous gestalt, and the solid-state macromolecule resin like perfluoro sulfonic acid type resin and perfluoro carboxylic acid type resin of the construction material generally used is desirable.

[0017] The fundamental cell structure of this invention is shown in drawing 1 . The fuel cell consists of the solid-state polyelectrolyte film 1, the hydrogen pole 2 and the oxygen pole 3 established in the both sides, and a charge collector 4 formed in the outside. Some gas supply slots are established in the charge collector 4. Two charge collectors 4 are opposed, an electrolyte membrane 1 and electrodes 2 and 3 are inserted between them, and a gas seal 5 protects the leakage of gas. Drawing 2 is the electrolyte membrane of drawing 1 , and the enlarged drawing of an electrode, and shows the arrangement relation between the hydrogen pole 2 of this invention, the oxygen pole 3, and the solid-state polyelectrolyte film 1. The hydrogen pole 2 consists of a catalyst bed 6 and a gaseous diffusion layer (it acts as an electronic conductor) 7, and the oxygen pole 3 consists of a catalyst bed 8 and a gaseous diffusion layer (it acts as an electronic conductor) 9. A gaseous diffusion layer can cast, sinter and obtain carbon fiber. An electrolyte membrane 1, a catalyst bed 6, the gaseous diffusion layer 7 and a catalyst bed 8, and the gaseous diffusion layer 9 are arranged as mentioned above, and application-of-pressure unification is carried out. Each catalyst bed mixes an active ingredient, carbon support, a proton conductor, and a water-repellent binder, casts and is obtained. An important thing is that the water repellence of a hydrogen pole is higher than the water repellence of an oxygen pole.

[0018] As mentioned above, while the wettability of a catalyst bed is controlled by the hydrogen pole and this invention promotes the electrode reaction within the pore of an electrode by raising the water repellence of a hydrogen pole rather than an oxygen pole Since the oxygen pole of a hydrophilic property is stronger and migration of moisture becomes easy, blowdown system outside of moisture becomes easy, and the cell engine performance is raised by improving the gaseous diffusion nature of two poles, and it is in having made it stabilize.

[0019] It may add in each catalyst bed and the binder with which water-repellent extent differs from the case where it carries out by changing the amount of a water-repellent binder and adding to a catalyst bed may be carried out to water-repellent control. It is the description that water repellence is controllable, without the former changing the pore structure of a catalyst bed. Although the latter changes some pore structures of a

catalyst bed, it is a simple and practical approach. Although the fluororesins [, such as polytetrafluoroethylene (PTFE),] and graphites fluoride represented with (CF) n , those mixture, etc. are usable as described above, it cannot include in a water-repellent binder so much from it being a resistor electrically. For example, when a water-repellent binder is polytetrafluoroethylene, the amount is 10 - 30 % of the weight preferably ten to 40% of the weight about an oxygen pole to the whole quantity of each catalyst bed of a hydrogen pole and an oxygen pole, and is 20 - 40 % of the weight preferably 20 to 50% of the weight about a hydrogen pole, and there are more the amounts of a hydrogen pole 10% of the weight or more in the difference than the amount of an oxygen pole. It is the range of an amount with the same said of other water-repellent binders. Although the ion exchange group of a proton conductor is hydrophilicity-like, it is not hydrophilicity-like [other parts] not necessarily. It changes with ingredients. Therefore, although the addition effectiveness of a proton conductor is not so remarkable as the case of water repellent, if an addition increases, a hydrophilic group will increase and a hydrophilic property will increase certainly. Thus, it is also possible to suppress the water repellence of the catalyst bed of an oxygen pole lower than that of the catalyst bed of a hydrogen pole.

[0020] The ion conductor for adding to a catalyst bed and aiming at amplification of effective reaction surface area has especially desirable high perfluoro sulfonic acid type resin or perfluoro carboxylic acid type resin of chemical stability etc. because of the severe service condition of touching oxidation and reducing atmosphere.

[0021] In order to prepare an electrode, the method of application is suitable. This approach mixes the carbon support catalyst which supported the active ingredient beforehand, a proton conductor, and a water-repellent binder, and consists of applying to the electronic conductor which is a gaseous diffusion layer. If an electrode is prepared by this approach, as mentioned above, the water repellence of an electrode prepares the addition of a water-repellent binder, and can select it to arbitration. Moreover, in order to form a water-repellent concentration gradient, a catalyst and a proton conductor are mixed, it applies on an electronic conductor, and the catalyst bed is formed. There is an approach of sinking into the front face of the catalyst bed the solution which distributed the water-repellent binder, or the approach of carrying out the laminating of the bilayer electrode with which water repellence differs, and unifying. Preparation of porosity is possible by changing the catalyst support, the water repellents, and those amounts of different particle diameter.

[0022] The catalyst bed which supported noble metals beforehand is formed in preparation of a catalyst component as a thin film in the shape of an electronic conductor. Furthermore, the approach of newly adding a noble-metals component from the front face is also good. It can be made to deposit as the approach in the impregnation of a noble-metals compound solution, plating, vacuum evaporation, ion implantation, etc.

[0023]

[Function] In a fuel cell, in order to promote desiccation prevention of an electrolyte membrane and migration of a proton in a hydrogen pole, moisture is added. When the water repellence of a catalyst bed is not enough, catalyst pore is covered with the moisture and diffusion of gas is checked. Moreover, since the movement magnitude of the moisture which moves into an electrolyte membrane will become imperfection and an electrolyte membrane will be in dryness when the water repellence of an oxygen pole is higher than a hydrogen pole, migration of a proton is checked, and the cell engine performance falls, without electrode reaction advancing. On the other hand, it is necessary to promote blowdown out of the system of the water of hydration which accompanies a proton, and the moisture generated by electrode reaction, and to raise the diffusibility of oxygen gas required for electrode reaction simultaneously on the oxygen pole.

[0024] In this invention, by making the water repellence of a hydrogen pole higher than an oxygen pole, the wettability of a hydrogen pole catalyst bed is controlled and excessive moisture was discharged out of the hydrogen pole catalyst bed. Therefore, makeup of sufficient moisture for an electrolyte membrane came to be carried out, and migration resistance of a proton was reduced, and blowdown of the water from an oxygen pole was promoted, and the flooding by water and generation water which are supplied from an electrolyte membrane is prevented. Consequently, amplification and stable maintenance of effective reaction area are attained, and the cell of high power density and the stable engine performance can be realized. However, making the water repellence of a hydrogen pole higher than an oxygen pole differs from the usual hydrogen-oxygen fuel cell. That is, hydrogen is superior to oxygen also in any of electrochemical labile and diffusibility. Therefore, it becomes the gaseous diffusion nature of an oxygen pole, and a technical problem important for engine-performance maintenance of reservation of reaction surface area, and it is devised so that the water repellence of an oxygen pole may be made high. However, in the solid-state macromolecule mold hydrogen-oxygen fuel cell, the operation effectiveness of this invention which is contrary to the

conventional common sense was accepted. However, since the lowness of the diffusibility of oxygen does not change even if there are particulars of a polymer electrolyte fuel cell, the water repellence of an oxygen pole cannot be made extremely low. There is a limitation naturally. When water repellent is PTFE, the minimum is 10 % of the weight.

[0025] The water repellence of a hydrogen pole catalyst bed is made for the solid-state polyelectrolyte film side to become low rather than a gaseous diffusion layer side. When the water repellence of an oxygen pole catalyst bed is made still lower than the solid-state polyelectrolyte side of a hydrogen pole catalyst bed and it was made for the water repellence of the gaseous diffusion layer by the side of an oxygen pole to turn into high water repellence from an electrode catalyst bed further. While promoting the flow of the water from a hydrogen pole to an air pole, encroachment of the water to a gaseous diffusion layer can be prevented, and a firedamp migration can be made easy. Moreover, the concentration of the proton conductor added to an electrode catalyst bed or the porosity of an electrode catalyst bed can adjust the water repellence of an electrode, or a hydrophilic property similarly. Since molecule size is small and the hydrogen supplied to a hydrogen pole has good diffusion when the porosity of an electrode catalyst is explained, diffusion of gas is easy in porosity being lower than an oxygen pole, and supply of gas does not become a defect. It is important to raise porosity, since the diffusibility of oxygen is low and reactivity is also low, and to supply sufficient amount on the oxygen pole. However, there is proper range in the porosity of an electrode, if porosity is too low, the diffusibility of gas will fall and electrode reaction will not advance. If porosity is too high, the electric resistance of an electrode catalyst bed will become high, further, it is easy to dry a catalyst bed with distributed gas, maintenance of the effective area of a reaction field becomes difficult, and the electrode engine performance stops moreover, being discovered. Therefore, there is proper range in porosity, according to the result of examination, the direction where 35 - 60% has [in] about 40 - 65 good% on the oxygen pole, and made the porosity of an oxygen pole higher than a hydrogen pole 5% or more is effective on the hydrogen pole on the water balance between two poles, but in order to raise the electrode engine performance, 10% or more is suitable.

[0026] Hereafter, although an example explains this invention, it is not limited to this.

[0027]

[Example]

The electrode catalyst which supported platinum to example 1 carbon powder was fully kneaded with the perfluoro sulfonic-acid system cation exchange resin (Aldrich Chemical shrine make, Nafion liquid) which is a proton conductor, and the drainage system suspension of PTFE, the paste was prepared, and it applied to about 100 micrometers of pore size and the carbon paper with a thickness of 100 micrometers which are an electronic conductor (gaseous diffusion layer). It was dried at 80 degrees C and the electrode was obtained. The above-mentioned electronic conductor is the drainage system suspension of PTFE to carbon paper PTFE coverage 12 mg/cm² It applied at a rate, and calcinated and obtained at 350 degrees C. The presentation of a hydrogen pole was set to 2 and 30 % of the weight of proton conductors with an amount [of platinum] of 0.3mg [/cm], and 30 % of the weight of PTFE. The presentation of an oxygen pole was set to amount of platinum 0.3 mg/cm², the 20 % of the weight of the same proton conductors as the above, and 20 % of the weight of PTFE.

[0028] The electrode made the same presentation as amount of platinum 0.3 mg/cm², 20 % of the weight of proton conductors, and 20 % of the weight of PTFE also with the hydrogen pole and the oxygen pole for this invention and a comparison was created as a conventional article for a comparison.

[0029] Adhesion on the solid-state polyelectrolyte film of the above electrode was performed by hot pressing. In an electrolyte membrane, it is Du Pont. Shrine make Nafion 117 It used. It is what allotted the hydrogen pole and the oxygen pole to the both sides of an electrolyte membrane 100kg/cm² It pressed at the temperature of 120 degrees C with the pressure for 15 minutes. A nest and the current density-voltage characteristic were measured for the electrode produced as mentioned above on condition that 80 degrees C and one atmospheric pressure in the measurement cel. The result is shown in drawing 3 .

[0030] the electrode 11 of a conventional type -- limiting current density -- 200mA/cm² it is -- things are shown -- receiving -- the limiting current density of the electrode 10 of this invention -- 450 mA/cm² It exceeded. Thus, by making the water repellence of a hydrogen pole higher than an oxygen pole, the cell engine performance was able to be improved substantially.

[0031] The preparation approach of example 2 electrode was as follows. The catalyst which supported platinum to carbon support, and the perfluoro carboxylic acid type resin which is a proton conductor were fully kneaded, and the catalyst paste was obtained. This paste was rolled out by the roll press, and two or more sheets were obtained. Impregnation of the PTFE drainage system suspension whose PTFE

concentration is 20 % of the weight was carried out to these sheets, it dried at 80 degrees C, and the sheet-like catalyst bed was obtained. Next, impregnation of the PTFE drainage system suspension which changed PTFE concentration into the sheet-like catalyst bed was carried out, and it dried at 80 degrees C.

Furthermore, impregnation of the PTFE drainage system suspension into which another PTFE concentration was changed was carried out, and it dried at 80 degrees C. Thus, the electrode with which a hydrogen pole and an oxygen pole have the concentration gradient of water repellent in the thickness direction of a catalyst bed was created. The water repellent concentration of the catalyst bed of a hydrogen pole has the concentration gradient so that it may become 40 % of the weight by the gaseous diffusion layer side 20% of the weight by the electrolyte side. The water repellent concentration of the catalyst bed of an oxygen pole had the concentration gradient so that it might become by the electrolyte membrane side and it might become 30 % of the weight by the gaseous diffusion side 10% of the weight. There was at least 10 % of the weight of differences of the water repellent concentration of a hydrogen pole and an oxygen pole.

[0032] The obtained sheet-like catalyst bed was united with carbon paper by the roll press, and the electrode was obtained. Hereafter, the same conditions as an example 1 compared. The obtained result is shown in drawing 4 . The curve 12 the cell engine performance of this invention indicates the cell engine performance of this invention to be to limiting current density is 2 500mA/cm. It exceeded. Thus, by giving a water repellent concentration gradient into the catalyst bed of a hydrogen pole and each oxygen pole showed that the cell engine performance improved substantially.

[0033] As it was three or less example, the electrode with which porosity differs between an electronic conductor, i.e., gaseous diffusion layer, side and an electrolyte side in each catalyst bed of a hydrogen pole and an oxygen pole was produced. Two poles were made two-layer, respectively. The electronic conductor side of the catalyst bed of a hydrogen pole kneaded the particle of the carbon support of 3 micrometers of mean diameters which ****(ed) platinum, 30% of the weight of ion exchange resin (perfluoro sulfonic acid type resin), and 40% of the weight of PTFE, and obtained the paste. This paste was applied to carbon paper and it dried at 80 degrees C. Furthermore, the paste which kneaded and obtained the particle of the carbon support of 1 micrometer of mean diameters which supported platinum, 30% of the weight of ion exchange resin, and 40 % of the weight of 40% of the weight of PTFE was applied on it, and it dried at 80 degrees C. Thus, the hydrogen pole which porosity made 50% by the electronic conductor side, and made 40% by the electrolyte membrane side was obtained. The catalyst bed of an oxygen pole applies to carbon paper the paste which kneaded and obtained the particle of the carbon support of 6 micrometers of mean diameters which supported the platinum catalyst, 20% of the weight of ion exchange resin (perfluoro sulfonic acid type resin), and 30% of the weight of PTFE. The paste which dried, obtained at 80 degrees C, and kneaded and obtained further the particle of the carbon support of 3 micrometers of mean diameters which supported the platinum catalyst on it, 20% of the weight of the same ion-exchange resin, and 30% of the weight of PTFE was applied to carbon paper, and it dried and obtained at 80 degrees C. Consequently, the porosity by the side of an electronic conductor of the porosity by the side of an electrolyte membrane was 60% 50%. It compared on the same conditions as an example 1. The obtained result is shown in drawing 5 . Limiting current density is 500 mA/cm² by the curve 13 which shows the cell engine performance of this invention. It turned out that it exceeds. Thus, by making the porosity of an oxygen pole higher than a hydrogen pole, the cell engine performance was able to be improved substantially.

[0034] It is possible to be able to improve more nearly substantially than the conventional thing the activity of the oxygen pole of a polymer electrolyte fuel cell and a hydrogen pole by this invention, and to obtain one about 2 to 3 times the output density of this so that clearly from the above result.

[0035]

[Effect of the Invention] The activity of the air (oxygen) pole of a solid-state polyelectrolyte mold hydrogen-air (oxygen) fuel cell can be improved by this invention more nearly substantially than the conventional thing, and the cell engine performance can be improved by leaps and bounds.

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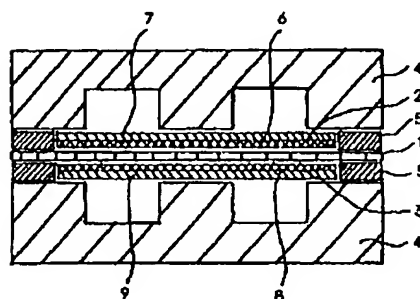
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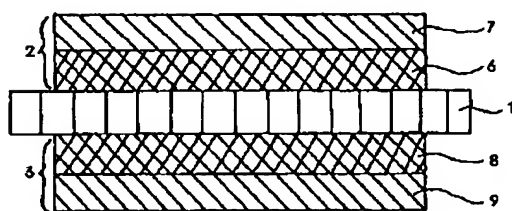
[Drawing 1]

図 1



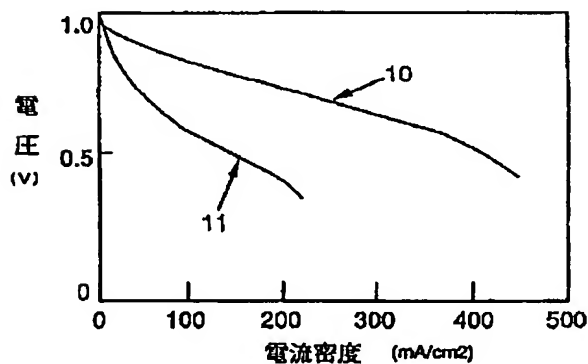
[Drawing 2]

図 2



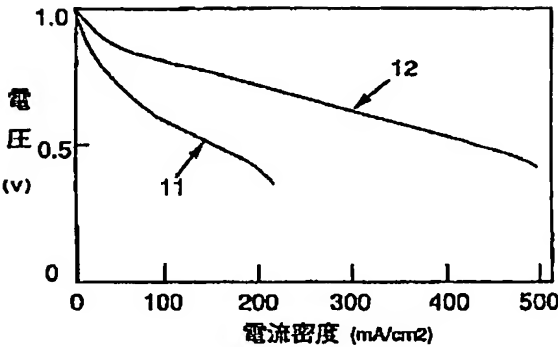
[Drawing 3]

図 3



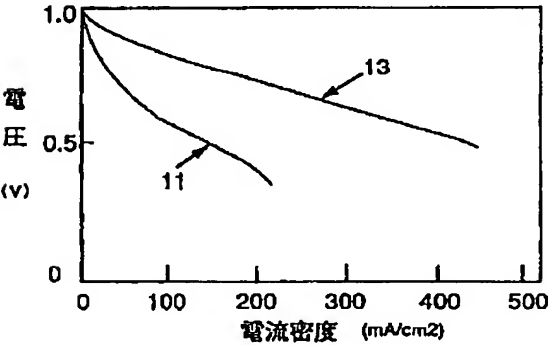
[Drawing 4]

図 4



[Drawing 5]

図 5



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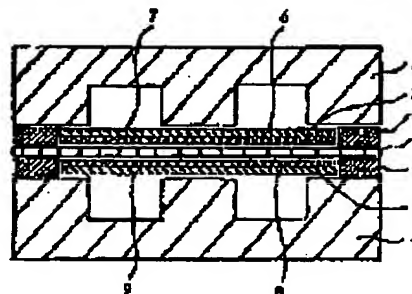
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(54) SOLID HIGHPOLYMER FUEL CELL

(57)Abstract:

PURPOSE: To greatly enhance the activity of an air electrode so as to significantly enhance the performance of a fuel cell having a hydrogen electrode and an air electrode provided on both sides of a film of solid highpolymer electrolyte by making the water repellency of the hydrogen electrode higher than that of the air electrode.

CONSTITUTION: A fuel cell comprises a hydrogen electrode 2 consisting of a catalyst layer 6 and a gas diffusion layer 7 with a film 1 of solid highpolymer electrolyte sandwiched therebetween, an oxygen electrode 3 consisting of a catalyst layer 8 and a gas diffusion layer 9, and a current collector 4 provided with several gas supply channels, and the end portion of each electrode 2, 3 is sealed by gas seals 5 to prevent gas leaks. Each of the catalyst layers is obtained by mixing and molding of an active component, a carbon carrier, a proton conductor and a water-repellent binding agent while the water repellency of the hydrogen electrode 2 is made higher than that of the oxygen electrode 3. Therefore, at the hydrogen electrode, electrode reactions in pores are accelerated, whereas at the oxygen electrode water is allowed to migrate easily and can readily be drained out of the system; so the gas diffusion properties of both of the electrodes are improved, resulting in enhancement of cell performance.



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[Kind of final disposal of application other than
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[Date of final disposal for application]

[Patent number] 2842150

[Date of registration] 23.10.1998

[Number of appeal against examiner's decision
of rejection]

[Date of requesting appeal against examiner's
decision of rejection]

[Date of extinction of right]

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(19) 日本国特許庁 (JP)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平 6 - 5 2 8 7 1

(43) 公開日 平成6年 (1994) 2月25日

(51) Int. Cl. ⁵	識別記号	庁内整理番号	F I	技術表示箇所
H 0 1 M	8/02	E 9062-4 K		
	4/86	H		
	8/10	9062-4 K		

審査請求 未請求 請求項の数 1 0

(全 6 頁)

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(54) 【発明の名称】 固体高分子型燃料電池

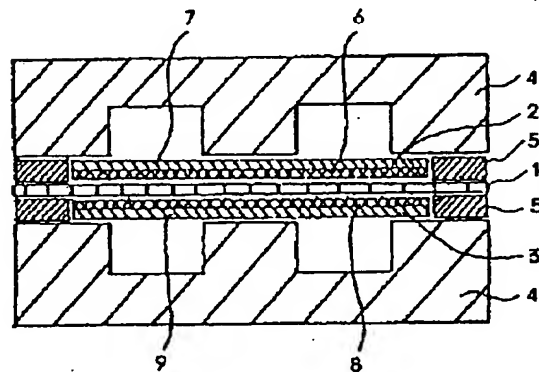
(57) 【要約】

【目的】 空気極と電解質との界面での水のフラッディングの防止、ガス拡散の促進と触媒活性表面の有効利用による電池出力特性の向上。

【構成】 固体高分子電解質膜の両側に水素極および空気極を設けた燃料電池において、空気極よりも水素極の撥水性を高くする。

【効果】 従来の電極に対して 2 - 3 倍の出力密度が得られる。

図 1



【特許請求の範囲】

【請求項 1】 固体高分子電解質膜と、その電解質膜を挟むように設けられたガス拡散電極である水素極及び酸素極と、水素含有ガス及び酸素含有ガスを該水素極及び該酸素極に供給する手段とを具備し、該ガス拡散電極が、カーボン担体と、それに担持された活性成分、プロトン伝導体及び撥水性結着剤とからなる触媒層及びガス拡散層を兼ねた電子伝導体とから構成され、該水素極側の触媒層の撥水性が該酸素極側の触媒層の撥水性よりも高いことを特徴とする固体高分子型燃料電池。

【請求項 2】 水素極の触媒層及び酸素極の触媒層の撥水性は、それぞれのガス拡散層側よりも固体高分子電解質膜側の方が低く、また、酸素極の触媒層の固体高分子電解質膜側の撥水性は、水素極の触媒層の固体高分子電解質膜側の撥水性より低いことを特徴とする請求項 1 に記載の固体高分子型燃料電池。

【請求項 3】 撥水性結着剤の量が、水素極及び酸素極のそれぞれの触媒層の全量に対して、酸素極については 10～40 重量％であり、水素極については 20～50 重量％であり、水素極のその量は酸素極のその量よりもその差において 10 重量％以上多いことを特徴とする請求項 1 に記載の固体高分子型燃料電池。

【請求項 4】 撥水性結着剤の量が、水素極及び酸素極のそれぞれの触媒層の全量に対して、酸素極については、10～30 重量％であり、水素極については 20～40 重量％であり、水素極のその量は酸素極のその量よりもその差において 10 重量％以上多いことを特徴とする請求項 1 に記載の固体高分子型燃料電池。

【請求項 5】 水素極の固体高分子電解質膜側の触媒層の撥水性結着剤の量は、酸素極の固体高分子電解質膜側のそれよりも、その差において 10 重量％以上多いことを特徴とする請求項 2 に記載の固体高分子型燃料電池。

【請求項 6】 水素極の触媒層が、酸素極の触媒層の気孔率よりも小さい気孔率を有することを特徴とする請求項 1 に記載の固体高分子型燃料電池。

【請求項 7】 気孔率が水素極の触媒層について 35～60％であり、酸素極の触媒層について 40～65％であることを特徴とする請求項 3 に記載の固体高分子型燃料電池。

【請求項 8】 酸素極の触媒層および水素極の触媒層はそれぞれ 2 層以上の多層であり、かつ各触媒層の中でガス拡散層側の方が撥水性が高いことを特徴とする請求項 1 に記載の固体高分子型燃料電池。

【請求項 9】 固体高分子電解質膜が、パーフルオロスルホン酸樹脂あるいはパーフルオロカルボン酸樹脂からなることを特徴とする請求項 1 に記載の固体高分子型燃料電池。

【請求項 10】 活性成分は、白金族金属からなることを特徴とする請求項 1 に記載の固体高分子型燃料電池。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は固体高分子型燃料電池に係り、特に固体高分子電解質型水素-酸素燃料電池に関する。

【0002】

【従来の技術】 固体高分子型燃料電池は、一般に 2 つの集電体と、固体高分子電解質膜（以下、単に「電解質膜」という）と、電解質膜を挟む 2 つの電極と、燃料としての水素及び酸化剤としての酸素を供給する手段とを具備する。両電極は触媒活性成分と、この触媒活性成分を担持する担体と、上記電解質と同じ固体高分子のイオン（プロトン）伝導体と、これらを固める結着剤とから構成された触媒層を有する。2 つの電極は水素極と酸素極とであり、それぞれにおける電気化学反応は次の通りである。

【0003】 水素極においては、水素分子がイオン化されてプロトンになり、電子を放出する。

【0004】 プロトンは電極内のイオン伝導体を伝導して、電解質膜に到達し、さらに電解質膜内を通過して、反対側の酸素極に移動する。一方、放出された電子は外部回路を通過して酸素極へ移動する。酸素極ではプロトンが水素極から放出された電子と結合して水が生成される。

【0005】 上記燃料電池の反応プロセスは主に次の 4 つの段階からなる。

【0006】 (A) 水素及び酸素の触媒表面への拡散、(B) 水素極及び酸素極内の触媒表面での反応、(C) プロトンの両極内部及び電解質内部における伝導、及び (D) 水の放出。

【0007】 それぞれの段階における燃料ガスの拡散の程度及び反応速度の程度が電池出力特性に大きく影響する。

【0008】 上記 (A) の段階では、燃料の触媒表面への供給及び拡散を効率的に行うことが有効であり、特開昭 60-35472 号公報の図 1 に示されているような波型集電体、特開平 3-102774 号公報又は特開平 2-86071 号公報等に開示されているような矩形溝を有するカーボンプレートを使用することが提案されている。これらの波型集電体や矩形溝を有するカーボンプレートの溝を有する側を電極に接触させると、接触面に空間が生じ、この空間を通して燃料が電極表面に拡散する。固体高分子型燃料電池では通常上記のような構造が採用されており、ある程度の出力が発現されている。

【0009】 電解質膜を通過してきたプロトンは、電解質膜と酸素極との界面で酸素との反応が進み酸素極界面では水が生成され、特に高電流密度では水膜が形成され、いわゆるフラッディング現象が生じる。この水膜のために電極内を拡散してきた酸素ガスと触媒との接触効率が低下し、出力密度の減少が起こり易くなり電池性能が不安定化する。このフラッディング現象は特に酸素極

と電解質の界面で生じやすい。そこでこの生成水を系外に除去する必要がある。

【0010】そのために米国特許第4,643,957号において電極の撥水性を制御してフラッディング現象を解消することを提案している。

【0011】

【発明が解決しようとする課題】本発明の目的は、水素極及び酸素極のガスの拡散を高い効率で行うため、水素極では水素分子から生成するプロトンの移動を促進させ、酸素極では水のフラッディングを防止し、電極触媒層とガスとの接触効率を向上するとともに、電極と電解質膜の界面で生じる酸化還元反応を加速する電極構造を有する、固体高分子型燃料電池を提供することである。

【0012】

【課題を解決するための手段】本発明は、固体高分子電解質膜とその電解質を挟むように設けたガス拡散電極である水素極及び酸素極と、水素含有ガス及び酸素含有ガスをそれぞれ水素極及び酸素極に供給する手段とを具備し、該ガス拡散電極は、カーボン担体と、それに担持された活性成分と、プロトン伝導体及び撥水性結着剤とからなる触媒層及びガス拡散層を兼ねた電子伝導体とから構成され、該触媒層の撥水性が、酸素極側よりも水素極側の方が高いことを特徴とする固体高分子型燃料電池である。

【0013】本発明によれば、各電極の触媒層の撥水性をある特定の条件下に制御することにより、固体高分子型燃料電池の電池性能を向上させることができる。

【0014】本発明の一例によれば、水素極の撥水性は、ガス拡散層よりも電解質膜の方が低く、また酸素極の触媒層内の撥水性も同様にガス拡散層よりも電解質膜側の方が低く、しかも水素極の触媒層の電解質膜側の撥水性よりも酸素極の触媒層の電解質膜側の撥水性の方が低い。なお、酸素極及び水素極の両方において、触媒層を1層にしても良いが、2層以上の多層でも良い。

【0015】本発明によれば、水素極及び酸素極の両極の触媒層は、カーボン担体とそれに担持された活性成分（触媒）、プロトン伝導体及び撥水性結着剤とからなる。活性成分は、白金又は白金族金属、例えば、ロジウム、ルテニウム、パラジウム及びイリジウムから選ばれることが好ましく、プロトン伝導体の材質は固体高分子電解質と同じであってもまた異なってもよい。また、撥水性結着剤はポリテトラフルオロエチレン（PTFE）などのフッ素樹脂又は（CF）_nで表されるフッ化黒鉛又はそれらの混合物が好適である。

【0016】本発明で使用する電解質は一般的に膜の形態であり、その材質は一般的に使用されるパーフルオロスルホン酸樹脂、パーフルオロカルボン酸樹脂のような固体高分子樹脂類が好ましい。

【0017】本発明の基本的な電池構造を図1に示す。燃料電池は固体高分子電解質膜1と、その両側に設けた

水素極2及び酸素極3と、その外側に設けた集電体4とからなっている。集電体4にはいくつかのガス供給溝が設けられている。2つの集電体4を向かい合わせてその間に電解質膜1と電極2、3とをはさみ、ガスシール5によりガスの漏れを防ぐ。図2は図1の電解質膜と電極の拡大図であり、本発明の水素極2と酸素極3と固体高分子電解質膜1との配置関係を示す。水素極2は、触媒層6とガス拡散層（電子伝導体として作用する）7とからなり、酸素極3は触媒層8とガス拡散層（電子伝導体として作用する）9とからなる。ガス拡散層は、たとえばカーボン繊維を成型し、焼結して得ることができる。電解質膜1、触媒層6とガス拡散層7、触媒層8とガス拡散層9を上記のように配置して加圧一体化する。各触媒層は活性成分、カーボン担体、プロトン伝導体及び撥水性結着剤を混合し、成型して得られる。重要なことは、酸素極の撥水性よりも水素極の撥水性の方が高いことである。

【0018】上記のように、本発明は酸素極よりも水素極の撥水性を高めることにより、水素極では触媒層の濡れ性が制御され、電極の細孔内での電極反応を促進させると共に、酸素極の方が親水性が強いいため、水分の移動が容易になることから、水分の系外排出が簡単となり、両極のガス拡散性を改善することで、電池性能を向上させ、かつ安定化させたことにある。

【0019】撥水性の制御には、撥水性結着剤の量を変化させて触媒層に添加して行う場合と、撥水性の程度が異なる結着剤をそれぞれの触媒層中に添加して行う場合とがある。前者は触媒層の細孔構造を変化させることなく撥水性を制御できることが特徴である。後者は触媒層の細孔構造を多少変化させるものの簡便で実用的な方法である。撥水性結着剤には、上記したように、ポリテトラフルオロエチレン（PTFE）などのフッ素樹脂、（CF）_nで代表されるフッ化黒鉛又はそれらの混合物等が使用可能であるが、電気的に抵抗体であることから、多量に含めることができない。たとえば、撥水性結着剤がポリテトラフルオロエチレンの場合、その量は水素極及び酸素極のそれぞれの触媒層の全量に対して、酸素極については10～40重量%、好ましくは10～30重量%であり、水素極について20～50重量%、好ましくは20～40重量%であり、水素極のその量は酸素極のその量よりもその差において10重量%以上多い。他の撥水性結着剤でも同様の量の範囲である。プロトン伝導体のイオン交換基は親水的であるがその他の部分は必ずしも親水的ではない。材料によって異なる。そのため、プロトン伝導体の添加効果は撥水剤の場合ほど顕著でないが、添加量が増加すれば親水基は増加し、確実に親水性が高まる。このようにして、酸素極の触媒層の撥水性を水素極の触媒層のそれよりも低く抑えることも可能である。

【0020】触媒層に添加して有効反応表面積の拡大を

図るためのイオン伝導体は、酸化および還元雰囲気に触れるという厳しい使用条件のため、化学的安定性の高いパーフルオロスルホン酸樹脂あるいはパーフルオロカルボン酸樹脂などが特に好ましい。

【0021】電極を調製するには、塗布方法が適している。この方法は、予め活性成分を担持したカーボン担体触媒、プロトン伝導体、撥水性結着剤を混合し、ガス拡散層である電子伝導体に塗布することからなる。この方法で電極を調製すると電極の撥水性は、上述のように、撥水性結着剤の添加量を調製して任意に選定できる。また、撥水性の濃度勾配を形成するには、触媒及びプロトン伝導体を混合し、電子伝導体上に塗布し触媒層を形成しておく。その触媒層の表面に撥水性結着剤を分散した溶液を含浸する方法、あるいは撥水性の異なる二層電極を積層して一体化する方法などがある。気孔率の調製は、異なる粒子径の触媒担体、撥水剤およびそれらの量を変化させることにより可能である。

【0022】触媒成分の調製には貴金属を予め担持した触媒層を電子伝導体上に薄膜として形成する。さらに、その表面から新たに貴金属成分を付加する方法も良い。その方法として、貴金属化合物溶液の含浸、めっき、蒸着、イオン打ち込み等で堆積させることができる。

【0023】

【作用】燃料電池においては、水素極には電解質膜の乾燥防止及びプロトンの移動を促進するために水分を添加している。触媒層の撥水性が十分でない場合は、その水分により触媒細孔がおおわれガスの拡散が阻害される。また、酸素極の撥水性が水素極よりも高い場合には電解質膜中へ移動する水分の移動量が不十分になり、電解質膜が乾燥状態になるのでプロトンの移動が阻害され、電極反応が進行せずに、電池性能が低下する。一方、酸素極ではプロトンと同伴する水和水と電極反応で生成する水分の系外への排出を促進させ、同時に電極反応に必要な酸素ガスの拡散性を向上させる必要がある。

【0024】本発明では、水素極の撥水性を酸素極よりも高くすることにより、水素極触媒層の濡れ性を制御し、余剰の水分は水素極触媒層外に排出するようにした。そのため、電解質膜には十分な水分の補給がされるようになり、プロトンの移動抵抗を低減し、また酸素極からの水の排出を促進し、電解質膜から供給される水や生成水によるフラッタイングを防止している。その結果、有効反応面積の拡大と安定維持が可能となり、高出力密度かつ安定な性能の電池が実現できる。しかし、水素極の撥水性を酸素極よりも高くすることは、通常の水素-酸素燃料電池とは異なる。すなわち、水素の方が酸素よりも電気化学的反応活性と拡散性のいずれにおいても優れている。そのため、酸素極のガス拡散性と反応表面積の確保が性能維持のために重要な課題となり、酸素極の撥水性を高くするように工夫されている。しかし、固体高分子型水素-酸素燃料電池では、従来の常識に反

するような、本発明の作用効果が認められた。しかしながら、固体高分子型燃料電池という特殊性はあっても、酸素の拡散性の低さは変わらないので、酸素極の撥水性を極端に低くすることは出来ない。おのずから限界はある。撥水剤がPTFEのときにはその下限は10重量%である。

【0025】水素極触媒層の撥水性をガス拡散層側よりも固体高分子電解質膜側の方が低くなるようにし、酸素極触媒層の撥水性を水素極触媒層の固体高分子電解質膜側よりもさらに低くし、さらに、酸素極側のガス拡散層の撥水性が電極触媒層よりも高撥水性になるようにしたことにより、水素極から空気極への水の流れを促進するとともに、ガス拡散層への水の浸入を阻止し、ガスの移動を容易にすることができる。また、電極触媒層に添加するプロトン伝導体の濃度、あるいは電極触媒層の気孔率等によっても同様に電極の撥水性ないしは親水性を調整できる。電極触媒の気孔率を説明すると、水素極に供給される水素は、分子サイズが小さく拡散が良いので、酸素極よりも気孔率が低くともガスの拡散は容易であり、ガスの供給が不良になることはない。酸素極では酸素の拡散性が低く、反応性も低いので気孔率を高めて、充分な量を供給することが重要である。しかし、電極の気孔率には適正範囲があり、気孔率が低過ぎるとガスの拡散性が低下し、電極反応が進行しなくなる。また、気孔率が高過ぎると電極触媒層の電気抵抗が高くなり、さらには、供給ガスにより触媒層が乾燥しやすく、反応場の有効面積の維持が困難になり電極性能が発現しなくなる。従って、気孔率には適正範囲があり、検討の結果によれば、水素極では35~60%が、酸素極では40~65%程度が良好であり、水素極よりも酸素極の気孔率を5%以上高くした方が、両極間の水バランスの上で効果があるが、電極性能を向上させるためには10%以上が適している。

【0026】以下、本発明を実施例により説明するが、これに限定されることはない。

【0027】

【実施例】

実施例1

カーボン粉末に白金を担持した電極触媒をプロトン伝導体であるパーフルオロスルホン酸系陽イオン交換樹脂(Aldrich Chemical社製、Nafion液)、およびPTFEの水系懸濁液とともに十分に混練してペーストを調製し、電子伝導体(ガス拡散層)である細孔径約100 μ m、厚み100 μ mのカーボンペーパーに塗布した。それを80℃で乾燥して電極を得た。上記電子伝導体は、カーボンペーパーにPTFEの水系懸濁液を、PTFE塗布量12mg/cm²の割合で塗布し、350℃で焼成して得た。水素極の組成は、白金量0.3mg/cm²、プロトン伝導体30重量%、PTFE30重量%とした。酸素極の組成は白金量0.3mg/cm²、上記と同じプロトン伝導体

20重量%、PTFE20重量%とした。

【0028】本発明と比較のために、水素極及び酸素極とも白金量0.3mg/cm²、プロトン伝導体20重量%、PTFE20重量%と同一組成にした電極を、比較対象の従来品として作成した。

【0029】以上の電極の固体高分子電解質膜への接着はホットプレス法により行った。電解質膜には、Du Pont社製 Nafion 117を用いた。水素極および酸素極を電解質膜の両側に配したものを100kg/cm²の圧力で温度120℃で15分プレスした。以上のように作製した電極を測定セルに組み込み、電流密度-電圧特性を80℃、1気圧の条件で測定した。その結果を図3に示す。

【0030】従来型の電極11は限界電流密度が200mA/cm²であることを示しているのに対して、本発明の電極10の限界電流密度は450mA/cm²を越えた。このように酸素極よりも水素極の撥水性を高くすることにより、大幅に電池性能を向上することができた。

【0031】実施例2

電極の調製方法は次の通りであった。カーボン担体に白金を担持した触媒とプロトン伝導体であるパーフルオロカルボン酸樹脂とを十分に混練して触媒ペーストを得た。このペーストを、ロールプレスで圧延して複数のシートを得た。これらのシートにPTFE濃度が20重量%のPTFE水系懸濁液を含浸させ、80℃で乾燥して、シート状触媒層を得た。次に、シート状触媒層にPTFE濃度を変えたPTFE水系懸濁液を含浸させ、80℃で乾燥した。更に、もう一つのPTFE濃度を変えたPTFE水系懸濁液を含浸させ、80℃で乾燥した。このようにして、水素極及び酸素極ともに触媒層の厚さ方向に撥水剤の濃度勾配がある電極を作成した。水素極の触媒層の撥水剤濃度は電解質側で20重量%、ガス拡散層側で40重量%となるように濃度勾配を有している。酸素極の触媒層の撥水剤濃度は、電解質膜側で10重量%、ガス拡散側で30重量%となるように濃度勾配を有した。水素極と酸素極の撥水剤濃度の差は少なくとも10重量%あった。

【0032】得られたシート状触媒層をカーボンペーパーにロールプレスで一体化し、電極を得た。以下、実施例1と同一条件で比較した。得られた結果を図4に示す。本発明の電池性能は、本発明の電池性能を示す曲線12から、限界電流密度は500mA/cm²を越えた。このように水素極および酸素極それぞれの触媒層内に撥水剤濃度勾配を与えることにより、電池性能が大幅に向上することが判った。

【0033】実施例3

以下のようにして、水素極及び酸素極のそれぞれの触媒層内において電子伝導体すなわちガス拡散層側と電解質側との間で気孔率の異なる電極を作製した。両極をそれ

ぞれ2層にした。水素極の触媒層の電子伝導体側は、白金を担持した平均粒径3μmのカーボン担体の粒子、30重量%のイオン交換樹脂（パーフルオロスルホン酸樹脂）及び40重量%のPTFEを混練して、ペーストを得た。このペーストをカーボンペーパーに塗布し、80℃で乾燥した。さらにその上に白金を担持した平均粒径1μmのカーボン担体の粒子、30重量%のイオン交換樹脂および40重量%のPTFE40重量%を混練して得たペーストを塗布し、80℃で乾燥した。このようにして、気孔率が電子伝導体側で50%、電解質膜側で40%にした水素極が得られた。酸素極の触媒層は、白金触媒を担持した平均粒径6μmのカーボン担体の粒子、20重量%のイオン交換樹脂（パーフルオロスルホン酸樹脂）及び30重量%のPTFEを混練して得たペーストをカーボンペーパーに塗布し、80℃で乾燥して得、さらにその上に、白金触媒を担持した平均粒径3μmのカーボン担体の粒子、20重量%の同じイオン交換樹脂及び30重量%のPTFEを混練して得たペーストをカーボンペーパーに塗布し、80℃で乾燥して得た。その結果、電解質膜側の気孔率は50%、電子伝導体側の気孔率は60%であった。実施例1と同じ条件で比較を行った。得られた結果を図5に示す。本発明の電池性能を示す曲線13により限界電流密度は500mA/cm²を超えることが分かった。このように水素極より酸素極の気孔率を高くすることにより、大幅に電池性能を向上することが出来た。

【0034】以上の結果から明らかなように、本発明により固体高分子型燃料電池の酸素極及び水素極の活性を従来のものより大幅に向上でき、約2〜3倍の出力密度を得ることが可能である。

【0035】

【発明の効果】本発明により固体高分子電解質型水素-空気(酸素)燃料電池の空気(酸素)極の活性を従来のものよりも大幅に向上でき、電池性能を飛躍的に向上できる。

【図面の簡単な説明】

【図1】本発明の燃料電池の模式断面図。

【図2】本発明の燃料電池用の固体電解質膜を挟む2つの電極の模式断面図。

【図3】本発明の実施例1による燃料電池の電流密度と電圧特性との関係を示すグラフ。

【図4】本発明の実施例2による燃料電池の電流密度と電圧特性との関係を示すグラフ。

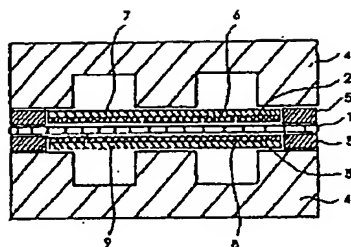
【図5】本発明の実施例3による燃料電池の電流密度と電圧特性との関係を示すグラフ。

【符号の説明】

1…固体高分子電解質膜、2…水素極、3…酸素極、4…集電体、5…ガスシール、6…水素極触媒層、7…ガス拡散層、8…酸素極触媒層、9…ガス拡散層。

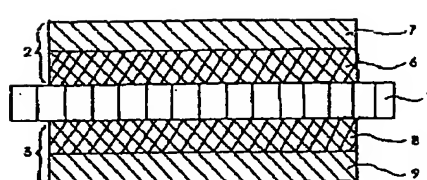
【図 1】

図 1



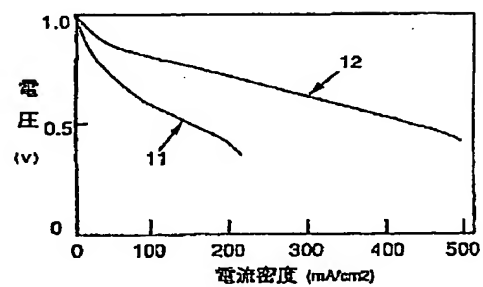
【図 2】

図 2



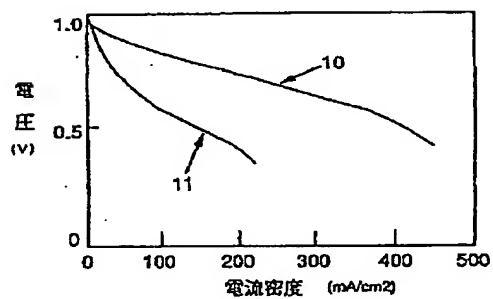
【図 4】

図 4



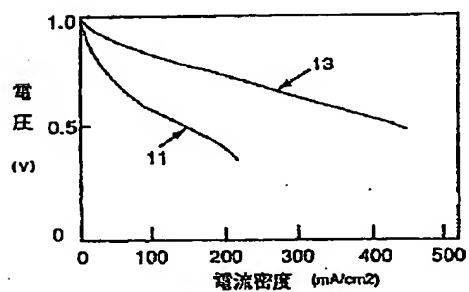
【図 3】

図 3



【図 5】

図 5



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